

INDIRECT LIQUEFACTION OF BIOMASS: A FRESH APPROACH

J.L. Cox, A.Y. Tonkovich, D.C. Elliott, E.G. Baker
Pacific Northwest Laboratory
Richland, Washington 99352

E.J. Hoffman
P.O. Box 1852
Laramie, Wyoming 82070

Keywords: gasification, liquefaction, biomass

INTRODUCTION

A variety of gaseous products for use as synthetic fuels and chemicals are produced by gasifying biomass. The actual product composition depends on the biomass composition and the reaction conditions. Several different gasification approaches have been investigated, at rather small scale, and reported in the literature (1,2). Many of these methods have their roots in coal gasification, including the work on catalytic gasification presented by Baker and Mudge (3) and Cox et al. (4). Catalytic gasification takes advantage of catalysts to serve two primary functions: 1) to increase the yield of gases, at the expense of tar and char, at lower temperatures than are possible without catalysts, and 2) to catalyze secondary reactions to produce the specific product desired. Sufficiently high rates can be achieved to allow operation at lower temperatures so that oxygen is not needed as a co-reactant, thus eliminating the need for an oxygen plant.

One catalytic approach to producing synthetic fuels and chemicals is indirect liquefaction of biomass, which entails gasifying the biomass to create a synthesis gas consisting of hydrogen and oxides of carbon. These materials, in turn, are converted to the desired liquid fuels and/or chemicals by suitable choice of catalyst, synthesis gas composition, and reaction conditions. This type of approach has been extensively investigated where coal is the carbonaceous feed material, but it has not been extended seriously to biomass and other feedstocks. It is generally recognized that developing gasification methods to produce the synthesis gas poses one of the major technical and economic challenges to improving this technology. This paper reports a different slant on indirect liquefaction that could stimulate advancements in the efficiency and economics of the process for biomass.

BIOMASS GASIFICATION - A NEW APPROACH

The new approach to biomass gasification outlined here is predicated on the concept that it is better to gasify biomass to a CO₂-synthesis gas composed primarily of H₂ and CO₂, rather than a CO-synthesis gas composed primarily of H₂ and CO. The conversion to CO₂-syn gas, and its subsequent utilization, may be superior, both technically and economically, to the route through a CO-syn gas.

A comparison of the stoichiometry of the respective routes is shown in Reactions (1) and (3), respectively.



Both carbon-steam (C-H₂O) gasification reactions are endothermic. The enthalpy of the C-H₂O reaction to produce CO-syn gas is 31.4 kcal/g-mole, while only 21.6 kcal/g-mole are required for the CO₂-syn gas reaction. The difference between the two reactions is the exothermic (-9.8 kcal/g-mole) CO-shift reaction given in Reaction (2). Clearly, biomass is not carbon; nevertheless, the conclusions are the same except the steam gasification of biomass is even more facile than carbon (i.e., graphite), and the thermodynamics are more favorable.

Minimizing the energy requirements for the gasification portion of the overall sequence in the indirect conversion to fuels and chemicals eases the burden of the most costly and inefficient step in the overall process. Pinto and Rogerson (5) report the cost of the reformer/gasmaking portion of a steam-reforming methanol plant constitutes 45% of the total capital cost. Henery and Louks (6) have shown that the economics of producing synthetic natural gas (SNG), i.e., methane, from coal and lignite depend strongly on the

cost of adding heat to the steam-carbon reaction. The amount of heat supplied and the method by which it is supplied to the gasification reactions are highly critical to the economics. In the case of SNG, Henery and Louks (6) estimate the cost of the gasification heat is 1/3 the cost of product (SNG). Any process that takes advantage of exothermic gasification reactions (e.g., $\text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2$ and $\text{C} + \text{H}_2 = \text{CH}_4$) in the gasifier can reduce external heat requirements and substantially improve process economics and efficiency. Calculations based on Reactions (1) and (3) indicate that CO_2 -syn gas requires 31% less energy to produce than CO-syn gas.

Another advantage of biomass in general is its reactivity allows sufficiently low temperatures ($<750^\circ\text{C}$) to be employed so that reaction enthalpy can be supplied indirectly by a tube still reactant heat exchanger. Consequently, there is no need for pure oxygen or a plant to produce it, and a major expense and energy penalty to the gasification section of the operating plant is eliminated.

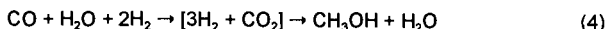
Because the reactivity of biomass varies among the different types (7,8), reaction conditions can be selected to favor the production of CO_2 -syn gas over CO-syn gas, including temperature, residence time, steam:biomass ratio, and the use of catalysts. The predicted gasification product composition is particularly sensitive to temperature and steam:biomass feed ratios. This sensitivity is shown in the equilibrium data in Table I, which indicate that the optimum conditions for producing CO_2 -syn gas are high steam:biomass ratio, low temperatures, and low pressures. At 1 atm, 600°C , and a steam:biomass (i.e., $\text{H}_2\text{O}:\text{C}$) mole ratio of 10:1, the product gas composition is 65.4% H_2 , 31.2% CO_2 , 3.0% CO , and 0.4% CH_4 . Since biomass has about 30 wt% oxygen, the amount of water required is predicted to be substantially less than 10:1.

While practically all gasification studies, irrespective of carbonaceous feedstock, have been conducted with the goal of producing CO-syn gas, there is sufficient experimental and theoretical evidence to suggest that, through reaction engineering principles, high conversions of feedstocks can be achieved, producing high yields of CO_2 -syn gas. Some of the predictions in Table I can be compared with experimental results under similar conditions shown in Table II.

CO- AND CO_2 - SYNTHESIS GAS CHEMISTRY

Work on the use of synthesis gas to produce a broad range of products began about 70 years ago in Germany with the production of fuels using cobalt catalysts (11-13). While this chemistry is loosely referred to as Fischer-Tropsch in recognition of the pioneering and extensive contribution of these individuals, there has been literally hundreds of significant contributors. The use of CO-syn gas has been the focus of this work, while CO_2 -syn gas has scarcely been considered.

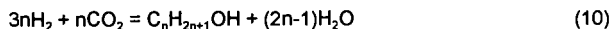
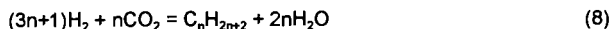
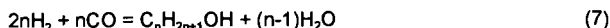
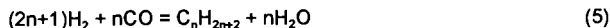
Table III illustrates the range of products that can be produced from CO-syn gas. Interestingly, optimum methanol synthesis over Cu/ZnO catalysts requires about 5% CO_2 in the inlet gas. If the CO_2 content is lower or higher, the methanol formation rate drops. Furthermore, the methanol formation apparently does not occur if the synthesis gas is free of CO_2 and H_2O . Russian investigators (18,19) have accounted for these observations by a mechanism where methanol formation is dominated by hydrogenation of CO_2 formed during reaction by the water gas shift reaction from CO:



Kuechen et al. (20) reported that a deactivated Cu/ZnO catalyst at 3-5 Mpa (30-50 atm) and 483-543K gave maximum rates of methanol synthesis with H_2 -CO- CO_2 syn gas ratio 70:0:30. The activation energy of methanol synthesis from CO_2 and H_2 was considerably lower than that from CO and H_2 . Cox et al. (4) reported the methanation of CO-free CO_2 -syn gas ($4\text{H}_2/\text{CO}_2$) in a packed bed reactor over supported nickel catalyst at 375°C , 100 psig, and space velocities of up to 7000 hr^{-1} .

REACTION COMPARISONS

Many of the synthesis schemes that have used CO-syn gas in the past appear to be possible using CO_2 -syn gas, as indicated here. The respective stoichiometries of aliphatic, olefin, and alcohol hydrocarbon formation from CO- and CO_2 -syn gases are shown in Reactions (5) through (10). The thermochemistry of some of the simpler homologs of these series of compounds is shown in Tables IVA and IVB. The data show that each are exothermic with favorable free energy changes at low temperatures and high pressures.



The advantage of using CO₂-syn gas in place of CO-syn gas may have significant overall process implications and, in some instances, reaction-specific benefits, as discussed below. For example, a comparison of the enthalpies of the CO- and CO₂-syn gases at 300°C shows the methanation to be about 18% less for the CO₂-syn gas (Reaction 8, n=1) than for CO-syn gas (Reaction 5, n=1), 35% less for the olefin formation (Reaction 9, n=2), 39% less for methanol formation (Reaction 10, n=1), and 29% less for ethanol formation (Reaction 10, n=2). Both CO- and CO₂-syn gas reactions are favored by pressure, but the CO-syn gas reactions are more favored than CO₂-syn gas. Comparative volume contractions for CO-syn gas versus CO₂-syn gas reactions are 50% versus 40% for methanation, 50% versus 37.5% for olefin formation, 66.5% versus 40% for methanol formation, and 66.7% versus 50% for ethanol formation. Hence, pressure can be used to considerable advantage to increase equilibrium conversions.

As expected from the enthalpies of reaction, the free energies are less for the respective CO₂-syn gas reactions. At 200°C, the respective free energy change (kcal/mole) for the CO- and CO₂-syn gas reactions are, respectively, -24.6 versus -19.5 for methanation, -13.46 versus -3.25 for olefin formation, 3.8 versus 8.9 for methanol formation, and -9.9 versus 0.3 for ethanol formation. For those reaction conditions with positive free energy changes, elevated pressures can be used to increase equilibrium yields, as is currently practiced in the commercial production of methanol from CO-syn gas. In the alcohol synthesis reactions, where free energy changes are not as favorable as for the other hydrocarbon synthesis reactions, higher pressures would be required to achieve equivalent equilibrium yields with the CO₂-syn gas.

Although some adjustments may be needed, these comparisons show the two synthetic gases to have comparable reactions for producing the desired products. Another salient feature of the new approach is that carbon deposition should not be the problem it is for CO-syn gas since the CO₂ counters the Boudouard reaction.



In addition, as can be seen from the thermodynamic data in Table IVB, synthesis reactions with CO₂-syn gas are less exothermic, reducing the difficulty of temperature control and expense of extra duty heat transfer equipment encountered when using CO-syn gas. Furthermore, lowering the concentration of CO alleviates a safety concern.

CONCLUSIONS

A new approach to indirect liquefaction of biomass is advocated based on the premise that it is easier to gasify the biomass to a CO₂-syn gas than to a CO-syn gas. Thermodynamic arguments are presented that show an energy savings of about 30%. Experimental data are presented that are consistent with the thermodynamic prediction that a CO₂-syn gas can be achieved through control of gasification conditions. Optimum gasification conditions are about 600°C, atmospheric pressure, and steam:biomass ratio equal to 10:1 in the presence of a gasification catalyst. The CO₂-syn gas under these conditions consists of 65.4% H₂, 31.2% CO₂, 3.0% CO, and 0.4% CH₄. Thermodynamic predictions have also been presented along with experimental results that indicate the range of products produced by catalytic conversion of CO₂-syn gas is comparable to products produced with CO-syn gas. Furthermore, carbon deposition and heat removal and temperature control are predicted to be more easily controlled with CO₂-syn gas chemistry. Even if catalytic conversion diversity with CO₂-syn gas is not as versatile as with CO-syn gas, the gasification to CO₂-syn gas represents an improvement in gasification efficiency, and the process can be used to produce fuel gas and hydrogen. While the discussion has focused on biomass, the concepts presented herein are appropriate for other carbonaceous materials such as coal and natural gas.

ACKNOWLEDGMENT

Pacific Northwest Laboratory is operated for the U.S. Department of Energy by Battelle Memorial Institute under Contract DE-AC06-76RLO 1830.

REFERENCES

- (1) Bridgwater, A.V. ed. *Advances in Thermochemical Biomass Conversion*. Blackie Academic & Professional/ Chapman Hall, Glasgow: 1994.
- (2) Overend, R.P.; Rivard, C.J. In *Proceedings First Biomass Conference of the Americas*, Vol. 1, pp. 471-497, 1993. NREL/CP-200-5768, National Renewable Energy Laboratory, Golden, Colorado.
- (3) Baker, E.G.; Mudge, L.K. *Catalysis in Biomass Gasification*. PNL-5030, Pacific Northwest Laboratory, Richland, Washington: 1984.
- (4) Cox, J.L. et al. *The Direct Production of Hydrocarbons from Coal-Steam Systems*. Research and Development Report No. 80, Office of Coal Research, U.S. Department of Interior: 1974.
- (5) Pinto, A.; Rogerson, P.L. *Chemical Engineering*, **1977**, 102-108.
- (6) Henery, J.P. Jr.; Louks, B.M. *Chem Tech.*, **1971**, 238-247.
- (7) Roberts, A.F. *Combustion and Flame*, **1970**, 14, 261-272.
- (8) Schiefelbein, G.F. "Biomass Gasification Research: Recent Results and Future Trends." PNL-SA-12841, Pacific Northwest Laboratory, Richland, Washington: 1985.
- (9) Lucchesi, A. et al. "Hydrogen by Pyrolysis-Gasification of Biomass." In *Proceedings of the Second International Symposium on Hydrogen Produced from Renewable Energy*, Cocoa Beach, Florida, October 22-24, 1985.
- (10) Mudge, L.K.; Baker, E.G.; Mitchell, D.H.; Robertus, R.J.; Brown, M.D. *Catalytic Gasification Studies in a Pressurized Fluid Bed Unit*. PNL-4594, Pacific Northwest Laboratory, Richland, Washington: 1983.
- (11) Storch, H.H.; Golumbic, N.; Anderson, R.B. In *The Fischer-Tropsch and Related Synthesis*. John Wiley & Sons: New York, 1951.
- (12) Pichler, H. In *Advances in Catalysis*. Frankenburg, W.G.; Komarewsky, V.I.; Rideal, E.K. eds., Academic Press: New York, 1952, Vol. 4.
- (13) Anderson, R.B. In *Catalysis*. Emmett, P.H. ed., Reinhold: New York, 1956, Vol. 4.
- (14) Mills, G.A.; Steffgen, F.W. *Catalysis Reviews*, **1973**, 8(2), 159-210.
- (15) Marschner, F.; Moeller, F.W. In *Applied Industrial Catalysis*. Leach, B.E. ed., Academic Press: New York, 1983, Vol. 2.
- (16) Hindermann, J. P.; Hutchings, G.J.; Kiennemann, A. *Catal. Rev.-Sci. Eng.*, **1993**, 35(1), 1-127.
- (17) Iglesia, E.; Reyes, S.C.; Madon, R.I.J.; Soled, S.L. *Adv. in Catalysis*, **1993**, 39, 221-302.
- (18) Rosovskii, A.Y. *Khim. Prom*, **1980**, 11, 652.
- (19) Kagan, Y.B. et al. *Kinet. Catal.*, **1976**, 17, 440.
- (20) Kuechen, C.; Hoffmann, U. *Chem. Eng. Sci.*, **1993**, 48(22), 3767-3776.

TABLE I. Predicted Equilibrium Gasification Product Compositions (1 atm)

Product, mol. %	500°C	600°C	700°C	800°C
<u>H₂O:C = 0.5</u>				
H ₂	38.1	49.3	50.9	49.8
CO ₂	36.8	25.1	11.1	2.9
CO	4.9	16.8	34.9	46.2
CH ₄	20.2	8.8	3.1	1.1
<u>H₂O:C = 1.0</u>				
H ₂	38.1	49.3	50.9	49.8
CO ₂	36.8	25.1	11.1	2.9
CO	4.9	16.8	34.9	46.2
CH ₄	20.2	8.8	3.1	1.1
<u>H₂O:C = 2.0</u>				
H ₂	38.1	50.7	57.1	57.1
CO ₂	36.8	25.3	17.2	14.4
CO	4.9	16.0	24.7	28.4
CH ₄	20.2	8.0	1.0	0.1
<u>H₂O:C = 3.0</u>				
H ₂	46.2	58.8	60.9	60.0
CO ₂	35.5	27.1	22.4	20.0
CO	3.9	10.9	16.4	20.0
CH ₄	14.4	3.2	0.3	0.0
<u>H₂O:C = 5.0</u>				
H ₂	56.9	63.8	63.2	62.6
CO ₂	33.8	29.3	26.9	25.0
CO	2.7	4.5	6.3	8.0
CH ₄	6.6	0.6	0.4	0.0
<u>H₂O:C = 10.0</u>				
H ₂	64.6	65.4	65.1	64.7
CO ₂	32.7	31.2	30.3	29.0
CO	1.5	3.0	4.6	6.3
CH ₄	1.2	0.4	0.0	0.0

TABLE II. Experimental Gasification Results

Feed Material	coal char	olive-husks	biomass
Catalysts	K ₂ CO ₃ /Ni-Al ₂ O ₃	none	Ni-Al ₂ O ₃
Steam/feed, lb/lb	3.8	-	5.7
Pressure, psia	30	15	15
Temperature, °C	560	747	735
SCF H ₂ /ton feed	90,000	35,000	not reported
Product(mol%, H ₂ O free)			
CO	1.9	6	5.8
CO ₂	36.6	25	29.9
H ₂	61.4	67	64.1
CO	1.9	6	5.8
CH ₄	0.0	2	0.2
Reference	4	9	10

TABLE III. Some Products Accessible Through CO-Synthesis Gas

Product	Reaction Conditions	Ref.
CH ₄	3H ₂ /CO, 350-400 °C, 50-100atm, 5,000-10,000 h ⁻¹ GSV, Ni/Al ₂ O ₃ Catalyst	14
CH ₃ OH	2H ₂ /CO, 230-300 °C, 50-100atm, Cu-ZnO Catalyst	15
C _n H _{2n+1} OH (n>1)	1.1H ₂ /CO, 260 °C, 130atm, 5,000-10,000 h ⁻¹ GSV, K-promoted MoS ₂ Catalyst	16
C _n H _{2n} (n=2-4)	1.4H ₂ /CO, 280 °C, 10atm, 340 h ⁻¹ GSV, Fe-Mn Catalyst	16
C ₅₊	2.1H ₂ /CO, 200 °C, 20atm, Co/SiO ₂ , 360 h ⁻¹	17

TABLE IVA. Comparative Thermochemistry of CO- and CO₂- Synthesis Gases (reactants and products in their normal states)

Reaction	Free Energy, kcal				
	25°C	200°C	250°C	300°C	350°C
5(n=1)	-36.04	-24.59	-21.78	-18.94	-16.06
6(n=2)	-31.48	-13.46	-9.34	-5.16	-0.95
7(n=1)	-6.97	3.76	6.64	9.56	12.50
7(n=2)	-32.89	-9.90	-4.17	1.60	7.40
8(n=1)	-31.26	-19.49	-17.15	-14.77	-12.34
9(n=2)	-21.92	-3.25	-0.07	3.18	6.49
10(n=1)	-2.19	8.86	11.27	13.73	16.22
10(n=2)	-23.34	0.31	5.09	9.94	14.85

TABLE IVB. Comparative Thermochemistry of CO- and CO₂- Synthesis Gases (reactants and products in their normal states)

Reaction	Enthalpy, kcal				
	25°C	200°C	250°C	300°C	350°C
5(n=1)	-59.78	-50.96	-51.38	-51.77	-52.13
6(n=2)	-71.26	-52.24	-52.76	-53.25	-53.70
7(n=1)	-30.63	-23.38	-23.72	-24.03	-24.31
7(n=2)	-81.83	-63.85	-64.34	-64.76	-65.13
8(n=1)	-60.47	-41.35	-41.88	-42.38	-42.85
9(n=2)	-72.64	-33.03	-33.76	-34.46	-35.13
10(n=1)	-31.32	-13.77	-14.22	-14.64	-15.02
10(n=2)	-83.21	-44.64	-45.33	-45.97	-46.56